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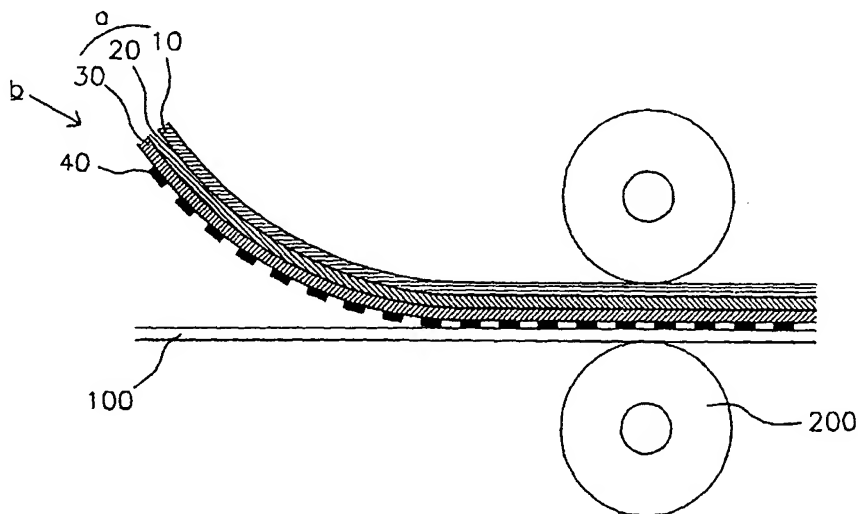
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(54) Title: PRINTING METHOD FOR THE SURFACE OF OBJECT



(57) Abstract: Disclosed is an adhesion printing method for integrally attaching a printed layer and a protective coated layer on a surface of a subject, comprising the steps of forming a print paper; forming a printed layer consisting of desired patterns on a graphic coated layer to form a printed paper; attaching the printed paper to the subject using heat of 200 to 250°C and a predetermined pressure such that the printed layer of the printed paper is positioned on the subject; and peeling a ground layer from the printed paper to form the print paper on the surface of the subject. The step of forming the print paper consists of the steps of coating a paper with silicone to form the ground layer; applying polyurethane resin liquid to the ground layer and hardening it to form a polyurethane resin layer; and forming the graphic coated layer on the polyurethane resin layer.

## PRINTING METHOD FOR THE SURFACE OF OBJECT

## TECHNICAL FIELD

5           The present invention relates, in general, to a method for printing various patterns on a surface of a subject and, in particular, an adhesion printing method for integrally attaching a printed layer and a protective coated layer on a surface of a subject, in which a printed paper integrally consisting of a coated layer for protecting the surface of the subject and improving texture of the subject, and a printed layer, is attached to the surface of the subject by applying  
10   heat and pressure, thereby printing is accomplished so that the subject has soft texture.

## PRIOR ART

          Generally, various types of patterns are printed on surfaces of sheet-type fibers, metal  
15   products, and cloths with the use of printing processes such as screen printing and gravier printing, or transfer processes using a sublimation dye. Various colors and patterns are printed on the subject using these printing processes, thereby increasing consumer demand for the printed products.

          Recently, artificial and natural leather having one color are disregarded by consumers,  
20   and so various colors and patterns are printed on the artificial and natural leather to gratify consumer's wants.

          A detailed description will be given of a conventional method for printing various colors and patterns on leather products, below.

          With respect to artificial leather, a surface of non-woven fabric or cloth is treated with  
25   chemicals, and then it is attached to artificial leather. Various patterns and colors are printed

on the surface of the non-woven fabric or cloth by use of the gravier printing process, and then a liquid coating is coated on the surface of the resulting non-woven fabric or cloth.

However, the above conventional method for printing artificial leather is disadvantageous in that resulting texture of artificial leather is poor. In other words, because patterns are separately printed on the sheet and the resulting sheet is attached to artificial leather, and then artificial leather is coated, a printed layer and a coated layer are formed on artificial leather. The printed layer is hardened by a hardening process and a coated layer on leather surface is also hardened, and so texture of artificial leather becomes poor.

In addition, the gravier printing process is disadvantageous in that the same number of copperplates as colors are needed to print desired patterns, workability is reduced because long time is needed to produce the copperplate, and time and expenses are greatly consumed because the copperplate is difficult to partially modify and the copperplate should be wholly modified even though a portion of the copperplate is required to be modified. Furthermore, because complicated and detailed patterns are difficult to print on leather by use of the copperplate, a high-priced article having complicated patterns cannot be obtained.

To avoid the above disadvantages, a sublimation transfer can be utilized. However, the sublimation transfer is not suitable for leather products because desired patterns are not clearly printed on leather, unlike fiber or cloth. That is to say, when patterns are printed on leather by use of the sublimation transfer, a sublimable dye applied to leather with the use of heat and pressure is penetrated inside of leather because of a permeability of leather, and so the sublimable dye is not clearly printed on the surface of leather. In addition, adhesion of ink to leather becomes poor because of occurring of a migration phenomenon with time. Furthermore, a paper is usually used as a release paper during the sublimation transfer. The paper firmly attached to leather by heat and pressure is difficult to remove from leather, and if the paper is removed, ink components are removed in conjunction with the release paper from

leather when the release paper is detached from leather.

As for natural leather, its surface should be separately pre-treated because it is preferable that patterns are not directly printed onto natural leather. Patterns are printed onto natural leather according to the same process as that is used for artificial leather, and so natural leather has the same disadvantages as artificial leather.

Meanwhile, products having the texture leather are regarded as high-quality products by consumers, and so if sheets such as synthetic fibers or cloths have the texture of leather as well as various patterns, consumer's wants can be inexpensively gratified. However, there does not exist a process for producing sheets such as synthetic fibers or cloths having the texture of leather by reforming the surface of the sheet.

The reason for this is due to limitations of a process for expressing patterns. When patterns are printed on synthetic fibers and cloths according to a graver or offset printing and a sublimation transfer, polyurethane resin liquid used to produce artificial leather should be firstly coated on the sheet such as the fiber or the cloth in order to express the texture of leather. In the case of using the graver printing process, in order to protect patterns printed on a polyurethane resin layer, a separate coating treatment should be conducted. Accordingly, the separate coating treatment causes print cost to be increased, and thus the resulting synthetic fibers and cloths become expensive. In addition, the synthetic fibers and cloths become poor in texture because of the coating treatment.

Directed to the sublimation transfer process, when patterns are printed on a sheet coated by the polyurethane resin liquid by sublimation transfer, the patterns are not clearly seen and ink components are not sufficiently attached to the sheet due to the migration phenomenon. In addition, sublimable dye is vaporized with time, and thus the pattern fades. Furthermore, if a paper is used as the release paper during the sublimation transfer, the paper is firmly bonded to the polyurethane resin liquid by heat and pressure, and so it is difficult for the paper to be peeled

from the polyurethane resin liquid, and if it is peeled from the polyurethane resin liquid, ink components are removed from the sheet in conjunction with the release paper.

In a conventional printing procedure, the surface of the subject is pre-treated or the resin liquid is coated on the subject, then patterns are printed on the resulting subject according to gravier printing, offset printing, or sublimation transfer, and thereafter a printed layer is separately coated for protecting patterns. The printing procedure should be sequentially conducted and the next phase is conducted after one phase is accomplished, therefore, large space and much time are needed to print patterns on the subject, and when the procedure is partially in error, the whole procedure is aborted.

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#### DISCLOSURE OF THE INVENTION

Therefore, it is an object of the present invention to avoid the above disadvantages, and to provide an adhesion printing method, in which various patterns are printed on a leather surface, and simultaneously leather surface is protected, as well as leather's texture being unchanged.

15

It is another object of the present invention to provide an adhesion printing method, in which a sheet such as synthetic fiber, resin, and cloth has a soft leather texture, and printing of patterns and protecting of the sheet's surface are simultaneously accomplished.

20

It is still another object of the present invention to provide a novel printing method, in which a patterned printed paper for protecting the surface of the subject is separately produced and printing is accomplished by only attaching the printed paper to the surface of the subject.

25

Based on the present invention, the above objects can be accomplished by provision of an adhesion printing method for integrally attaching a printed layer and a protective coated layer on a surface of a subject, comprising the steps of forming a print paper; forming a printed

layer consisting of desired patterns on an upper side of a graphic coated layer of the print paper to form a printed paper; attaching the printed paper to the surface of the subject using heat of 200 to 250°C and a predetermined pressure such that the printed layer of the printed paper is positioned on the surface of the subject; and peeling a ground layer from the printed paper to form the print paper on the surface of the subject. The method can simultaneously form patterns and a protective layer on the surface of the subject, and the step of forming the print paper consists of the steps of coating a surface of a paper with silicone to form the ground layer; applying polyurethane resin liquid to the ground layer and hardening it to form a polyurethane resin layer for protecting patterns; and forming the graphic coated layer, on which patterns will be printed, on an upper side of the polyurethane resin layer.

Preferably, an adhesive layer is additionally formed on the surface of the subject by coating the adhesive on the subject and hardening the adhesive.

The ground layer coated with silicone is formed by coating silicone liquid with a viscosity of 250 to 450 cps on one side or both sides of the paper and drying the silicone liquid at 120 to 180°C for 2 to 5 min.

The polyurethane resin layer is formed by coating liquid with the viscosity of 100000 to 170000 cps on the ground layer and hardening the liquid, wherein the liquid is produced by mixing 25 to 35 wt% of polyurethane having a molecular weight distribution of 100000 to 150000 with 65 to 75 wt% of a solvent, and the polyurethane is produced by reacting diisocyanate with polyol having a molecular weight distribution of 1000 to 5000.

The graphic coated layer is formed by coating liquid with the viscosity of 100000 to 170000 cps on the polyurethane resin layer and hardening the liquid, wherein the liquid is produced by mixing 15 to 25 wt% of polyurethane having a molecular weight distribution of 100000 to 150000 with 75 to 85 wt% of an organic solvent, and the polyurethane is produced by reacting diisocyanate with polyethylene glycol. In addition, the graphic coated layer may

further comprise 1 to 5 wt% of porous silicone.

It is preferable that the organic solvent further comprises 5 to 10 % toluene so as to improve a dispersibility of polyurethane resin.

## 5 BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

10 Fig. 1 is a sectional view of a printed paper according to the present invention;

Fig. 2 illustrates a heat pressing procedure of the printed paper attached to a surface of artificial leather;

Fig. 3 illustrates a heat pressing procedure of the printed paper attached to a surface of natural leather; and

15 Fig. 4 is a sectional view of the printed paper attached to a surface of synthetic fibers.

## BEST MODES FOR CARRYING OUT THE INVENTION

According to the present invention, a printed paper comprising a protective layer for  
20 protecting an outer side of a patterned printed layer and capable of expressing the texture of leather is separately produced. The printed paper is attached to artificial and natural leathers with applying heat and pressure. The resulting leather retains the texture of leather and is improved in quality because the protective layer protects patterns. Furthermore, the printed  
paper showing the texture of leather may be attached to sheets such as synthetic fibers, resins,  
25 and cloths, thereby high-quality sheets having the texture of leather as well as various patterns

can be obtained.

That is to say, in the present invention, the printed paper showing the texture of leather as well as various patterns and capable of protecting the printed layer should be separately produced.

3 A detailed description of the production process of the printed paper will be given, below.

Fig. 1 is a sectional view of a printed paper according to the present invention. As shown in Fig. 1, the printed paper b comprises a print paper a consisting of a ground layer 10, a polyurethane resin layer 20, and a graphic coated layer 30; and a printed layer 40 forming  
10 patterns on the print paper a.

The ground layer 10 generally used during a sublimation transfer is peeled from a surface of leather after being attached to the surface of leather. However, the ground layer 10 of the present invention is different from the conventional ground layer usually used during the sublimation transfer in that the conventional ground layer consists of only a paper, but the  
15 ground layer 10 of the present invention consists of a paper 10a coated with silicone 10b so as to be peelable. Generally, a polyurethane resin liquid is used to produce artificial leather. However, the polyurethane resin has a strong bonding strength and is firmly bonded to the paper used as the ground paper, and thus when the conventional ground paper is used, the ground paper has poor releasability, and ink components are removed when the paper is peeled  
20 from leather.

Accordingly, in order to avoid the above disadvantages, the ground layer 10 should not be reacted with the polyurethane resin and ink components, nor subjected to temperatures of about 200 °C or higher. Thus, silicone resin liquid 10b is coated onto the ground layer 10a. The silicone resin liquid is coated on one side of the ground layer on which patterns will be  
25 printed, and preferably, on both sides of the ground layer.



The ground layer is coated with silicone according to the following procedure.

A general yellow paper 10a is used as a ground paper 10a. Silicone resin liquid 10b with a viscosity of 250 to 450 cps is coated on the yellow paper. At this time, the silicone resin liquid 10b is coated on one side or both sides of the yellow paper 10a. The yellow paper 10a,  
5 on which the silicone resin liquid 10b is coated, is dried at about 120 to 180°C for 2 to 4 min so that the silicone resin liquid 10b is sufficiently hardened on the yellow paper 10a, thereby the resulting ground layer 10 is produced.

In addition to the ground layer 10 thus produced, a release paper may be used for embossing patterns on the surface of leather. In other words, because patterns are embossed  
10 on the whole ground paper 10a and leather is attached to the release paper, the embossed patterns on the release paper can be formed on the surface of leather. A detailed description of the release paper will be omitted because the release paper is widely used for embossing patterns on leather.

As for a polyurethane resin layer 20, it acts as a protective layer for protecting a  
15 printed layer 40 as will be described below and a layer for showing the texture of leather. The polyurethane resin layer 20 is composed of the same material as resin liquid used during the production of artificial leather. Accordingly, the polyurethane resin layer 20 can show the texture of leather when the polyurethane resin layer is used on synthetic fibers and cloths as well as leather. In addition, the polyurethane resin layer 20 acts as a protective layer for protecting  
20 the printed layer 40, as will be described later because the polyurethane resin layer 20 is positioned over the outer surface of the printed layer 40.

The polyurethane resin layer 20 is produced according to following procedure.

First of all, diisocyanate monomer is reacted with polyol to produce the polyurethane resin. Polyol has a molecular weight of about 1000 to 4000, and preferably polyester polyol or  
25 polyether polyol with a molecular weight distribution of about 1000 to 4000 is used as polyol.

The polyurethane resin thus produced has the molecular weight distribution of 100,000 to 150,000. For example, when the polyurethane resin has the molecular weight distribution of 100,000 or lower, physical properties of the polyurethane resin become poor because bonding force between molecules in the polyurethane resin is seriously weakened after being hardened.

- 5 On the other hand, when the polyurethane resin has the molecular weight distribution of 150,000 or higher, the polyurethane resin is too hard to use as the polyurethane resin layer.

The polyurethane resin is used with its viscosity being controlled after the polyurethane resin is dissolved in a solvent to form a liquid phase resin. Examples of the solvent include MEK or DMF, which is generally used as the solvent of polyurethane resins, and the viscosity of a solution of the polyurethane resin in the solvent ranges from 110,000 to 160,000 cps at 25 °C. The polyurethane resin of 30 to 40 wt % is mixed with the solvent of 60 to 70 wt % so that the viscosity of the solution of the polyurethane resin in the solvent is within the above range.

Then, the polyurethane resin layer 20 should be sufficiently aged because a graphic coated layer 30, to be described later, should be completely separated from the polyurethane resin layer 20 so that patterns are clearly shown. That is to say, if the graphic coated layer 30 is coated on the polyurethane resin layer 20 while the polyurethane resin layer 20 is not sufficiently aged, the polyurethane resin layer 20 is chemically reacted with the graphic coated layer 30, and so the printed layer 40 is not sufficiently formed. On the other hand, if the graphic coated layer 30 is coated on the polyurethane resin layer 20 after the polyurethane resin layer 20 is sufficiently aged, the printed layer 40 is properly formed. Preferably, after the polyurethane resin liquid with its viscosity being controlled is coated on the ground layer, the polyurethane resin is left at room temperature for at least 24 hours to sufficiently age.

With respect to the graphic coated layer 30, it acts as a layer for forming the printed layer 40, and can form patterns according to various printing processes. Water-based ink

generally used in a printer is suitable to protect an environment, form various patterns, use in small quantity batch production, and clearly form complicated patterns. When patterns are printed through the printer using the water-based ink, amendment and compilation of patterns can be easily conducted. Additionally, oil-based-ink for gravier or offset printing used in mass  
5 production and a sublimable dye used in a sublimation transfer may be applied to the graphic coated layer.

After being coated on the polyurethane resin layer, the resulting subject should sufficiently show the texture of leather and not changed in physical properties by the graphic coated layer 30. Furthermore, the graphic coated layer 30 should be firmly bonded to the  
10 polyurethane resin layer 20, i.e. the protective layer for protecting the resulting subject, so as not to be detached from the polyurethane resin layer.

To form the preferable graphic coated layer, ink components should be sufficiently permeated into the graphic coated layer, and so the graphic coated layer should have a porosity after being hardened.

15 In order to produce porous polyurethane, diisocyanate monomer is reacted with polyol having a molecular weight distribution of 1500 to 4000, and preferably with polyol consisting of polyethylene glycol. The polyethylene glycol used for producing the porous polyurethane has a water-soluble property. Therefore, when used in a printing process, the polyethylene glycol is easily reacted with the water-based ink, and so the printing process is easily  
20 accomplished. The porous polyurethane resin produced by reacting diisocyanate with polyol has the molecular weight distribution of 100,000 to 150,000.

The polyurethane resin is used while it is dissolved in a solvent. The solvent is selected from the group consisting of a hydrophilic solvent and a lipophilic solvent. When the water-based ink is used as the printing ink, the hydrophilic solvent is used so that the solvent is  
25 easily reacted with the water-based ink. On the other hand, when the oil-based ink is used as

the printing ink, MEK used as the solvent of the polyurethane resin may be used. It is preferable that IPA, that is, a solvent in which 90 to 95 % IPA is mixed with 5 to 10 % toluene, is used as the hydrophilic solvent. The toluene is added to IPA so as to improve dispersibility, and cause the polyurethane resin to be uniformly dispersed in the hydrophilic solvent. When  
5 too much toluene is added to IPA, physical properties of the graphic coated layer become poor, while the dispersibility of the polyurethane resin is improved.

Meanwhile, a separate porous silica may be added to mixed liquid of the solvent and the polyurethane in order to easily print patterns on the subject. The porous silica has a porosity and added to a mixture of the solvent and the polyurethane resin during production of  
10 the mixture. The porous silica is in powder type solid and is uniformly dispersed into the polyurethane resin liquid, and so the silica sufficiently contains the printing ink. However, when too much porous silica is added to the polyurethane resin liquid, physical properties of the graphic coated layer become poor because the polyurethane resin layer becomes rigid, and so it is preferable that silica of about 1 to 3 wt % is added to the polyurethane resin.

15 Additionally, a dispersant, an ultraviolet absorption agent, an antioxidant, and an amine-based catalyst may be added to the polyurethane resin liquid, in a small amount. These chemicals have been widely used in formation of films using polyurethane resin, and so a detailed description of these chemicals will be omitted. Meanwhile, in order to produce the graphic coating liquid, the solvent of 75 to 85 wt % is mixed with the polyurethane resin of 15  
20 to 25 wt % in a reactor at 40 to 60°C for 10 hours or more.

The printed layer 40 is a layer for forming various patterns, and formed using a print paper a consisting of the ground layer 10, the polyurethane resin layer 20, and the graphic coated layer 30. The print paper a has the texture of leather, and patterns are formed on the print paper a.

25 When patterns are edited by use of a computer and then output through a printer, the

print paper a is used as a paper for the printer, and so the printed layer 40 having patterns printed by the water-based ink is formed on the graphic coated layer 30 of the print paper a, thereby a printed paper b according to the present invention is completed.

5 In the case of using gravier or offset printing process, patterns printed by the oil-based ink are formed on the graphic coated layer 30 of the print paper a, and in the case of using a sublimation transfer, a sublimable dye is transferred into the graphic coated layer 30 of the print paper a. That is to say, desired patterns and colors are formed in the printed layer 40 by use of various printing processes, and patterns in the printed layer 40 are formed on the surface of leather by attaching the print paper a to leather.

10 A procedure for forming various colors and patterns by use of the printed paper b comprising the printed layer 40 positioned on the print paper a and the print paper a will be described with reference to the accompanying drawings.

According to a first embodiment of the present invention, patterns are printed on artificial leather.

15 As shown in Fig. 2, the print paper a consisting of the ground layer 10, the polyurethane resin layer 20, and the graphic coated layer 30 is produced according to the above procedure. The print paper a is used as the paper for the printer, desired patterns are edited by a computer, and edited patterns are output through the printer. Patterns are printed on the graphic coated layer 30 by use of the water-based ink to form the printed layer 40. In the case  
20 of using gravier or offset printing process, the printed layer 40 is formed on the print paper a to produce the printed paper b.

The printed layer 40 of the printed paper b is put on the surface of artificial leather 100, and the resulting artificial leather 100 passes through roller 200. While the resulting artificial leather passes through the roller 200, the printed paper b is attached to the surface of  
25 artificial leather 100 by pressure and heat of 220°C. The printed paper b is completely

attached to the surface of artificial leather 100 by heat. In detail, the surface of artificial leather 100 consists of the polyurethane resin, and also the graphic coated layer 30 mostly consists of the polyurethane resin, and thus the graphic coated layer 30 is firmly bonded to the surface of artificial leather 100 by heat and pressure. The printed layer 40 is positioned between the graphic coated layer 30 and the surface of artificial leather 100, and so the printed layer 40 is not easily peeled away. Furthermore, because the polyurethane resin layer 20 for protecting the printed layer 40 and showing the texture of leather is formed on the outer side of the graphic coated layer 30, the printed layer 40 is more protected.

After the printed paper b passing through the roller 200 is attached to the surface of artificial leather 100, the ground layer 10 is peeled from the polyurethane resin layer 20. As described above, the ground layer 10 is coated with silicone. The silicone has a high resistance to heat and is not reacted with the polyurethane resin, and so the ground layer 10 is easily peeled from the polyurethane resin layer 20. Because the peeled ground layer 10 is not damaged during use, it can be reused without producing additional ground layers, and so production cost of the ground layer 10 is reduced.

As described above, patterns are well protected because patterns are positioned on the surface of artificial leather 100, and the graphic coated layer 30 and the polyurethane resin layer 20 are covered on the patterns. In addition, patterns can be formed while the texture of leather does not become poor because the graphic coated layer 30 and the polyurethane resin layer 20 has the texture of leather, and the two layers are integrally attached to each other. The resulting artificial leather was tested for quality of leather, as follows.

- Color fastness to washing (tested by FITI Testing & Research Institute and Korea Institute of Footwear & Leather Technology)

1) Samples were tested according to a standard method of FITI Testing & Research Institute (BS 1006 C06 A2, single test 40°C, 30 min, 0.4 % ECE Reference detergent, 0.1 %

sodium perborate tetrahydrate), and when the color fastness to washing of samples is ranked as 4 or higher, they can be used as commercial products.

Artificial leather produced according to the first embodiment of the present invention was compared to commercial polyester, acryl, and wool in terms of the color fastness to washing, and the results are as follows: color fastness to washing of artificial leather of the present invention: 4.5; color fastness to washing of polyester: 4.5; color fastness to washing of acryl: 4.7; and color fastness to washing of wool: 4.3.

By the above results, it can be seen that color fastness to washing of artificial leather of the present invention is sufficient for use as commercial leather.

2) Samples were tested according to a standard method of Korea Institute of Footwear & Leather Technology (ASTM D 0430,  $40 \pm 1^\circ\text{C}$ , 30 min, water 100 ml, Ball 10ea, Soaf 5 g/l), and when the color fastness to washing of samples is ranked as 4 or higher, they can be used as commercial leather.

Artificial leather produced according to the first embodiment of the present invention were compared to commercial polyester, acryl, and wool in terms of the color fastness to washing, and the artificial leather of the present invention was ranked as 5 in terms of color fastness to washing; and additionally, the comparative polyester, acryl, and wool were also ranked as 5, and therefore the artificial leather of the present invention can be used as commercial leather.

- Color fastness to light (UV test)

Samples were tested according to standard methods of 1) FITI Testing & Research Institute (KS K0700 Fade-o-meter, ISO Blue Scale, carbon arc lamp), 2) Korea Institute of Footwear & Leather Technology (ASTM D 1148 300W X 10 inch,  $40 \pm 1^\circ\text{C}$ , 24 hours), and results were evaluated to be 4 or higher in both leathers, therefore the artificial leather of the present invention can be used as commercial leather.

In addition, the leather of the present invention is same as commercial products in terms of color fastness to dry cleaning, dyeing color fastness to rubbing, color fastness to rubbing, and heat resistance.

From the above results, it can be seen that artificial leather according to the present invention has various patterns positioned on a surface thereof while texture of artificial leather is not damaged. Therefore, according to the present invention, various patterns can be easily and inexpensively printed on artificial leather in small quantity batch production, and complicated and detailed patterns can be printed on artificial leather.

According to a second embodiment of the present invention, patterns are printed on natural leather, as shown in Fig. 3. The surface of natural leather 100' is different from the surface of artificial leather in terms of chemical components. The surface of artificial leather is composed of polyurethane resin, while natural leather does not comprise polyurethane resin. Accordingly, the printed paper b is attached to the surface of natural leather after the surface of natural leather 100' is pre-treated.

In other words, the surface of natural leather 100' is pre-treated so that a graphic coated layer 30 of the printed paper b is attached to the surface of natural leather 100'. In a pre-treatment of natural leather 100', an adhesive c is used for attaching the printed paper b to natural leather 100', and preferably, a polyurethane resin based adhesive is used for constantly maintaining physical properties of the graphic coated layer. However, an adhesive layer is only several  $\mu\text{m}$  in thickness, and so a general adhesive may be used for attaching the printed paper b to natural leather 100'.

Because the polyurethane resin based adhesive c has the same physical properties as the polyurethane resin layer 20 coated on the printed paper b, and preferably acts as the adhesive between the printed paper b and natural leather 100' while the texture of leather does not become poor. Furthermore, the polyurethane resin based adhesive c has good reactivity,



and thus it is easily coated on the surface of natural leather 100' and firmly bonded to the surface of natural leather without changing of physical properties. Additionally, the polyurethane resin based adhesive c should be sufficiently aged so as to smoothly react with the graphic coated layer 30.

5           After the polyurethane resin based adhesive c is coated on the surface of natural leather 100', patterns are printed on natural leather according to the same procedure as the first embodiment of the present invention. Therefore, the adhesive layer c formed on the surface of natural leather 100' acts as the adhesive between the printed paper b and natural leather 100', and natural leather according to the second embodiment of the present invention can have  
10       various patterns while the texture of leather does not become poor.

          According to a third embodiment of the present invention, sheets such as synthetic fibers, resins, cloths, and non-woven fabrics are treated so as to have various patterns and the texture of leather, thereby the sheet is upgraded as the high value-added commercial sheet.

          As described above, because synthetic fibers and cloths are composed of polymeric  
15       materials, patterns can be printed on synthetic fibers and cloths by a general sublimation transfer. However, they have not the texture of leather. Accordingly, the surface of the sheet should be reformed so as to show soft the texture of leather. In the third embodiment, the adhesive consisting of polyurethane resin may be coated on the sheet such as fiber and cloth, or the sheet may be used without adhesives. For example, because a reactivity of the sheet such  
20       as polyester and wool with urethane resin is good, the sheet can be used without a separate adhesive layer. However, in the case of using the sheet such as nylon based resin, it is preferable that the adhesive layer is coated on nylon based resin for firmly bonding the sheet to the urethane resin. As described above, because the polyurethane resin based adhesive is thin in thickness and has the texture of leather, the sheet having the adhesive positioned on the  
25       surface thereof does not become poor in the texture of leather.

Patterns are printed on the surface of the sheet, which is coated with the adhesive or not, by use of the printed paper of the present invention, by the same procedure as the first embodiment. After patterns are printed on the surface of the sheet, the printed layer 40 is formed in conjunction with the graphic coated layer 30 on the surface of the sheet 100'' such as fiber and cloth, and the polyurethane resin layer 20 is positioned on the outer side of the graphic coated layer 30, as shown in Fig. 4. The resulting sheet has the texture of leather as well as various patterns, thereby consumer's wants can be inexpensively gratified.

According to a fourth embodiment of the present invention, patterns are printed on the surface of natural leather through a different procedure from the second embodiment.

In the second embodiment, the surface of natural leather is pre-treated with the use of the adhesive. According to the fourth embodiment, however, ink components are permeated inside of the surface of natural leather 100' by a sublimation transfer. At this time, patterns are integrally formed with leather, and thus patterns can be constantly shown when the surface of natural leather is worn.

According to the fourth embodiment of the present invention, patterns are formed on the printed paper b by water-based ink used in the sublimation transfer. After that, the printed paper b is attached to the surface of natural leather 100' and then aged while being pressed. In more detail, the printed paper attached on the surface of natural leather is wound on a roll. At this time, heat is transferred through the roll to natural leather, thereby the sublimation transfer is accomplished. The printed paper attached on the surface of natural leather, which is heated and pressed, is aged under atmosphere while being wound on the roll.

The sublimation transfer is not completely accomplished only by heating and pressing natural leather and the printed paper positioned on natural leather, but it is completed after the resulting natural leather is aged for about 14 to 18 hours while leather being wound on the roll.

That is to say, if natural leather is drawn and the ground paper is removed after natural

leather is sufficiently aged while being wound on the roll, the printing ink is sufficiently transferred to the surface of natural leather and is firmly bonded to natural leather.

As described above, the printed paper showing the texture of leather is separately produced in the present invention. Accordingly, various patterns are formed on the printed paper regardless of a subject, and the printed paper is separately used to print patterns on a surface of the subject at need, thereby workability is improved. In other words, the printed paper is separately produced and the printed paper thus produced can be directly applied to various products because division of labor is feasible, thereby devices for printing patterns on natural leather become simple.

Furthermore, because the printed paper is separately produced, and printing is accomplished by only attaching the printed paper thus produced to the subject using heat and pressure, products having constant quality can be produced without variation of physical properties.

## INDUSTRIAL APPLICABILITY

As described above, the present invention is advantageous in that various patterns can be printed on surfaces of artificial and natural leather, and the texture of leather is maintained, as well as a pattern protective layer being formed. Other advantages of the present invention are that sheets such as synthetic fibers and cloths can be inexpensively changed into high-quality products because the sheets can have a soft texture of leather and various patterns on a surface thereof, devices for printing patterns on natural leather become simple, and products having constant quality can be produced without variation of physical properties because the printed paper is separately produced and the printed paper thus produced can be directly applied to various products.

The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended  
5 claims, the invention may be practiced otherwise than as specifically described.

## CLAIMS

1. An adhesion printing method for integrally attaching a printed layer and a protective coated layer on a surface of a subject, comprising the steps of:

5       forming a print paper, consisting of the steps of:

coating a surface of a paper sheet with silicone to form a ground layer;

applying polyurethane resin liquid to the ground layer and hardening the resin liquid to form a polyurethane resin layer for protecting patterns; and

forming a graphic coated layer, on which patterns will be printed, on an upper side of  
10 the polyurethane resin layer;

forming a printed layer consisting of desired patterns on an upper side of the graphic coated layer of the print paper to form a printed paper;

attaching the printed paper to the surface of the subject using heat and pressure such that the printed layer of the printed paper is positioned on the surface of the subject; and

15 peeling the ground layer from the printed paper to form the print paper on the surface of the subject,

whereby said method is able to simultaneously form patterns and a protective layer on the surface of the subject.

20       2. The adhesion printing method according to claim 1, wherein the attaching step is conducted at 100 to 200°C for 2 to 4 minutes with the printed paper being attached to the surface of the subject.

25       3. The adhesion printing method according to claim 1, wherein the printed paper attached to the surface of the subject is pressed at a temperature of 50 to 80°C, wound, and aged

at a room temperature for 10 to 20 hours, in the attaching step.

4. The adhesion printing method according to claim 1, wherein an adhesive layer is additionally formed on the surface of the subject by coating a liquid adhesive on the surface of the subject and hardening the liquid adhesive.

5. The adhesion printing method according to any one of claims 1 to 4, wherein the ground layer coated with silicone is formed by coating a silicone liquid with a viscosity of 250 to 450 cps on one side or both sides of the paper sheet and drying the silicone liquid at 120 to 180°C for 2 to 5 minutes.

6. The adhesion printing method according to claims 1 or 2, wherein the polyurethane resin layer is formed by coating a polyurethane resin liquid with a viscosity of 100000 to 170000 cps on the ground layer and hardening the polyurethane resin liquid, said polyurethane resin liquid being produced by mixing 25 to 35 wt% of polyurethane having a molecular weight distribution of 100000 to 150000 with 65 to 75 wt% of a solvent, said polyurethane being produced by reacting diisocyanate with polyol having a molecular weight distribution of 1000 to 5000.

7. The adhesion printing method according to claim 6, wherein the polyol comprises polyester polyol or polyether polyol.

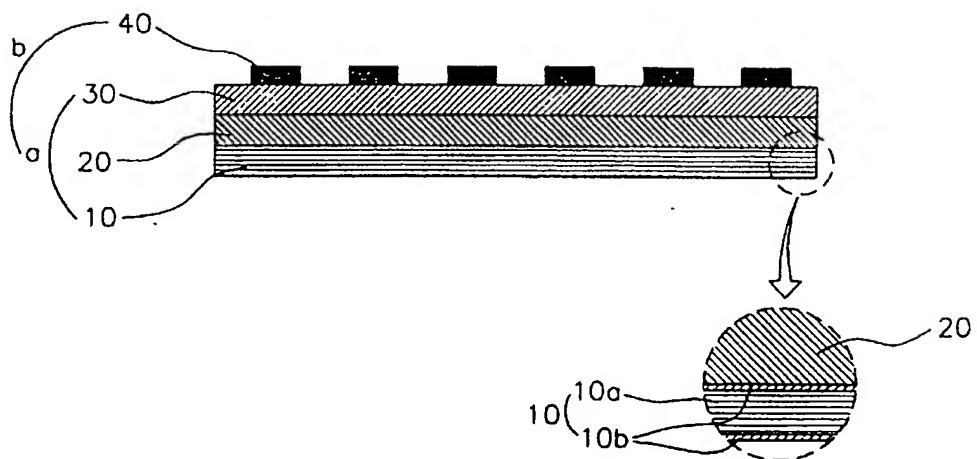
8. The adhesion printing method according to any one of claims 1 to 4, wherein the graphic coated layer is formed by coating a polyurethane resin liquid with the viscosity of 100000 to 170000 cps on the polyurethane resin layer and hardening the polyurethane resin

liquid, said polyurethane resin liquid being produced by mixing 15 to 25 wt% of polyurethane having a molecular weight distribution of 100000 to 150000 with 75 to 85 wt% of an organic solvent, said polyurethane being produced by reacting diisocyanate with polyethylene glycol.

5           9. The adhesion printing method according to claim 8, wherein the graphic coated layer further comprises 1 to 5 wt% of porous silicone.

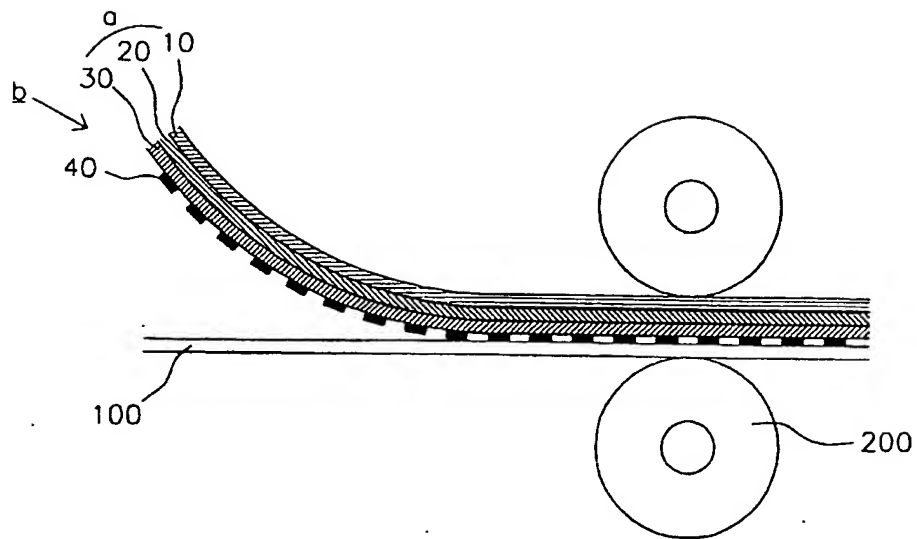
10. The adhesion printing method according to claim 8, wherein the organic solvent further comprises 5 to 10 % of toluene so as to improve a dispersibility of polyurethane resin.

1 / 4  
FIG. 1

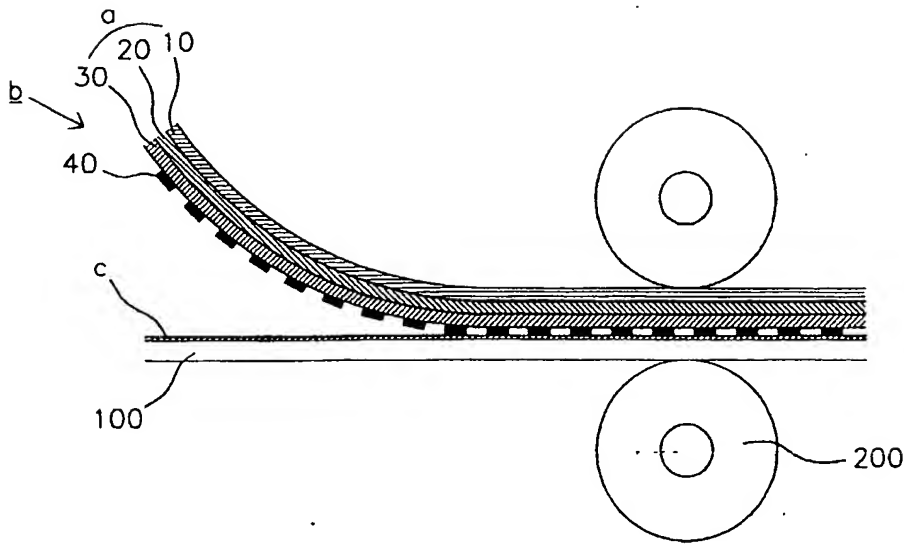




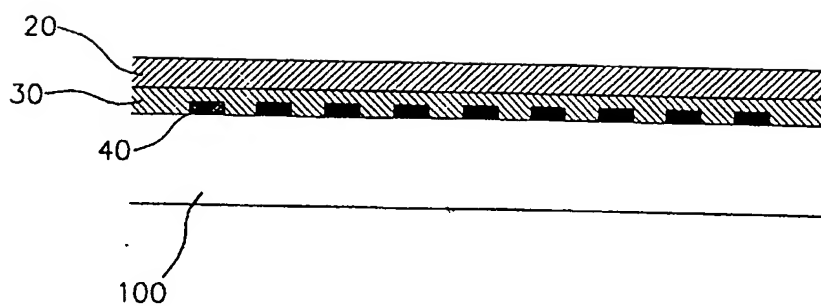
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FIG. 2



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FIG. 3



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FIG. 4



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR01/02271

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC7 B41M 5/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC7 B41M D06N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 2000-42496 A (LEE, GEOL GU) 15 JULY 2000	1, 2, 4
Y	KR 1998-74787 A (SUH, CHUNG KIL) 05 NOVEMBER 1998	1
A	KR 2000-12374 A (RO, DO SEONG) 06 MARCH 2000	1
A	KR 2000-61767 A (SHINWOO HI-TECH CO., LTD.) 25 OCTOBER 2000	1
A	KR 1990-8686 B (DAI NIPPON PRINTING CO., LTD. et al) 26 NOVEMBER 1990	1
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A	US 5,593,940 A ((DAI NIPPON INSATSU KABUSHIKI KAISHA) 14 JANUARY 1997	1
A	US 5,885,928 A (DAI NIPPON PRINTING CO., LTD. ) 23 MARCH 1999	1
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search		Date of mailing of the international search report
24 APRIL 2002 (24.04.2002)		25 APRIL 2002 (25.04.2002)
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